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AB INITIO TREATMENT OF LARGE MOLECULES

REINHART AHLRICHS, SIMON D. ELLIOTT AND UWE HUNIAR
Lehrstuhl für Theoretische Chemie, Universität Karlsruhe
Institut für Physikalische Chemie und Elektrochemie
Kaiserstr. 12, 76128 Karlsruhe
Germany
E-mail: ramail@tchibm3.chemie.uni-karlsruhe.de, simon.elliott@tcd.ie
uwe@tchibm3.chemie.uni-karlsruhe.de

We give a brief exposition of the fundamental approximations of ab initio calculations, the SCF, DFT and MP2 methods for calculating molecular wavefunctions and energies are introduced. The Resolution of Identity (RI) approach is described with a view to the treatment of large molecules (100 atoms and more). Scaling behavior of the various computational methods is compared; here, aluminium clusters represent a demanding application. The utility of analytical energy gradients is shown, in particular using the example of a theoretical study of the structural isomers of sulfur-bridged copper clusters. A strategy to compute electronic excitation energies for large molecules is sketched and applications to fullerenes and cadmium-selenide nanoclusters are presented. Developments in scientific computing hardware are considered, with emphasis on the emergence of PC's. The opportunities and difficulties inherent in the parallelization of quantum chemical code are also discussed, and the performance of parallel TURBOMOLE is presented.

1 Introduction

Computing in the natural sciences and engineering has gained considerably in importance as a result of the ever increasing power of available hardware. As a consequence it is justified to speak of the tripod of science: experiment, theory and scientific computing. The first two of these branches should not require an explanation. The third, scientific computing, comprises "computer experiments" which give exact results - up to rounding errors and errors in computer programs - within a model ultimately defined by the computational procedures applied, i.e. by the assumptions on which they are based. The better the model and the justification for assumptions, the better and the more realistic the results. Scientific computing thus permits the prediction and checking of results of experiments and especially their interpretation. This clearly will never make experiments superfluous - but it will change and has already changed the way in which experiments are designed and selected. We just remind the reader of the importance of computer modelling in the design of air planes, jet engines, cars, and computers, in oil exploration and weather forecasting, to name just a few fields essentially shaped by modern simulation techniques.

In the present article we deal with molecular electronic structure theory [1,2], the application of Quantum Mechanics to determine properties - "observables" - of molecular systems. The central problem is here the approximate but sufficiently accurate solution of the molecular Schrödinger equation. This is a formidable task, a real grand challenge, simply because of the dimensionality: the wavefunction describing a system of 100 electrons and nuclei is a function of 300 cartesian coordinates (all problems mentioned above are three-dimensional cases), which is simply

not manageable in an accurate way. Despite these apparently insurmountable difficulties, chemists now almost routinely perform calculations for systems with a few hundred atoms, which give results that are competitive in accuracy and effort with measurements. Some aspects of this methodology will be sketched in this article, where "large molecules" are those with of the order of 100 atoms and more.

2 The Zoo of Methods

2.1 The Standard Approximations: MO-LCAO-CGTO [2]

We separate the treatment of electrons and nuclei by means of the Born Oppenheimer approximation and are then left with the electronic Schrödinger equation. Approximate ab initio treatments are almost invariably based on the variation principle which requires an evaluation of

$$E[\psi] = \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle \tag{1}$$

$$H = \sum_i h(i) + \sum_{i<j} 1/r_{ij} \tag{2}$$

The one-electron terms h include the kinetic energy of electrons and their interaction with the nuclei; in the two-electron terms r_{ij} denotes the distance between electrons i and j. We have sufficient knowledge of properties of exact wavefunctions to guess a high quality ansatz for ψ, but it is then impossible to evaluate the $3n$-dimensional integrals in (1), n = number of electrons, with sufficient accuracy and reasonable effort. The structure of high quality wavefunctions has been extensively probed in treatments of small atoms and molecules, especially He and H_2.

An application of the variation principle requires an ansatz for ψ for which integration is easy in general: all integrals should factorize into low dimensional cases. This is achieved by building ψ from the one-electron functions φ_i called molecular orbitals (MO), and this leads to the general configuration interaction (CI) ansatz

$$\psi = \sum_I C_I \Phi_I \tag{3}$$

$$\Phi_I = [\varphi_{i1}...\varphi_{in}] \tag{4}$$

$$\langle\varphi_i|\varphi_j\rangle = \delta_{ij} \tag{5}$$

The square brackets in (4) indicate the assignment of spins and antisymmetrization, the formation of Slater determinants.

As a result of (3)-(5), the evaluation of $E[\psi]$ is reduced to simple three and six-dimensional integrals

$$h_{ij} = \int \varphi_i h \varphi_j d\tau^3 \tag{6}$$

$$(ij|kl) = \int \varphi_i(r_1)\varphi_j(r_1)1/r_{12}\varphi_k(r_2)\varphi_l(r_2)d\tau^6 \tag{7}$$

This solves the problem of integration. However, the number of configurations to be included in (3) to achieve a prescribed accuracy basically grows exponentially with the size of the system: CI treatments are in general not feasible for large molecules at present.

The MO ansatz makes an application of the variation principle possible; efficiency of an implementation depends on the actual representation of MO's φ_i. The success of Quantum Chemistry is essentially based on the use of Gaussian functions: the MO's φ_i are approximated as "linear combinations of atomic orbitals" (LCAO) f_μ

$$\varphi_i = \sum_\mu C_{\mu i} f_\mu \tag{8}$$

and the atom centered basis functions f_μ are "contracted Gauss type orbitals" (CGTO)

$$f_\mu = \left\{ \sum_\gamma d_\gamma exp(-\eta_\gamma r^2) \right\} \mathrm{Mon}(x, y, z). \tag{9}$$

$\mathrm{Mon}(x, y, z)$ denotes a monomial, i.e. Mon = 1 for an s function, Mon = x or y or z for p functions and so on. The fixed parameters in (9) - contraction coefficients d_γ and exponents η_γ - have typically been optimized in calculations of atoms. If (8) is plugged into (6) and (7) one is left with integrals $h_{\nu\mu}$ and $(\nu\mu|\kappa\lambda)$, defined in complete analogy to (6) and (7) by replacing φ_i by f_ν, etc. These integrals $h_{\nu\mu}$ and $(\nu\mu|\kappa\lambda)$ over Gaussians are simple analytic expressions which can be evaluated very efficiently: around 20 additions and multiplications per primitive integral.

2.2 Single Determinant Wavefunctions: SCF and DFT

The simplest MO ansatz includes only a single term, $\psi_{SCF} = \Phi_1$, in the CI expansion (3). This is a crude approximation and reasonable results can only be expected if the MOs occupied in ψ_{SCF} are variationally optimized: the Self-Consistent Field (SCF) approach. Despite its simplicity this is a very useful approximation. Equilibrium structure constants of most main group compounds are obtained with errors of about 2% in bond distances and a few degrees in bond angles; simple examples are discussed in [2]. Exceptions are mainly found for weak bonds like those in F_2 or the N-N bond in N_2O_4 where errors can be considerably larger. We leave it to the reader to compare this with the accuracy of experimental structure determinations typically achieved in the gas phase or in crystals for large molecules. The SCF approach is useless for binding energies but reaction energies can be computed to within 10 kJ/mol for isodesmic and especially homodesmic reactions. The SCF approximation also fails for molecules containing transition metals; only cases that are formally d^0 can be treated since they more or less behave as main group elements.

Many deficiencies of the SCF approach are rectified by density functional theory (DFT) methods. DFT is easy to characterize if one takes a very pragmatic attitude. Choosing for simplicity a closed shell system, we write the SCF energy expression as

$$E_{SCF} = E^{(1)} + J - E_x \tag{10}$$

$$E^{(1)} = 2\sum_i h_{ii} \tag{11}$$

$$J = 2\sum_{ij}(ii|jj) = \frac{1}{2}\int \rho(r_1)1/r_{12}\rho(r_2)d\tau^6 \tag{12}$$

$$E_x = \sum_{ij}(ij|ij) \tag{13}$$

$$\rho(r) = 2\sum_i |\varphi_i(r)|^2 = \sum_{\nu\mu} D_{\nu\mu} f_\nu(r) f_\mu(r)\ . \tag{14}$$

In a remarkable paper Kohn and Sham established - a correct proof was given later by others - the existence of an "exchange correlation" functional $E_{xc}[\rho]$ such that [3,4]

$$E_{DFT} = E^{(1)} + J - E_{xc}[\rho] \tag{15}$$

yields the exact density ρ and the exact ground state energy, $E_{DFT} = \mathrm{E}_0$, provided (15) is minimized with respect to the MO's φ_i. The exact functional $E_{xc}[\rho]$ is unknown, also unknown are systematic procedures to derive (better and better) functionals from the exact Schrödinger equation. Approximate functionals are thus derived from a study of the underlying physics, by considerations of model systems, and by simple fits (e.g fitting E_x to SCF results for atoms or to experimental data). The dominant contribution to E_{xc} is, of course, the Dirac approximation for exchange: $E_x \approx \mathrm{const} \cdot \int \rho^{4/3} d\tau^3$.

This pragmatic approach to determining exchange correlation functionals has been very successful. DFT yields much improved energetics for main group compounds [5]. Even more importantly, DFT methods also yield reasonable results for transition metal compounds and metal clusters for which SCF is essentially useless. There are still problems: DFT quite consistently overestimates bond distances and the density vanishes too slowly at larger distances from nuclei.

DFT has repeatedly been characterized as an essentially semiempirical method, quite recently by Handy and coworkers [6]. If one accepts this judgement, one has to add that DFT introduces a new quality of semiempirical procedures since the level of reasoning and the foundation of the approximations are on a much higher level than for example for CNDO or MNDO and its variants.

2.3 MP2: Second Order Perturbation Corrections to SCF

The only other method presently applicable to large molecules is MP2 (Møller-Plesset second order pertubation correction) which adds the dominant effects of electron correlation to the SCF treatment. Two comments about MP2 should be made. MP2 is the first term of a perturbation expansion based on SCF as zeroth order. There is no way to establish or estimate the convergence properties of this series in general. MP2 typically improves SCF if the latter is already a useful approximation, and errors with respect to experiment or reliable high level calculations are reduced to roughly 30% (compared to SCF), e.g. in NMR chemical shifts [7]. Applicability is thus restricted to most of main group chemistry, transition metals with d^0 and in addition with d^{10} atomic states. The other comment concerns basis sets: MP2 requires use of (much) larger basis sets than needed for SCF. MP2 treatments require, in addition to a preceeding SCF calculation, the computation of two-electron integrals $(ia|jb)$, e.g. (7), for all pairs of occupied (i, j) and virtual (a, b) MO's. The computational effort is thus much larger than for SCF.

2.4 Gradient Techniques and Properties [8]

The development of techniques to evaluate analytical gradients, i.e.

$$E_\lambda^{(1)} = \partial E/\partial\lambda \tag{16}$$

$$E_{\lambda\mu}^{(2)} = \partial^2 E/\partial\lambda\partial\mu \tag{17}$$

of the electronic energy (SCF, DFT, MP2, etc.) with respect to external parameters (λ, μ) has been essential for the success of Quantum Chemistry. The programs for (16) and (17) are clearly more complicated than those for the corresponding energy - but one gets used to it: last year's sensation is this year's calibration. Analytical gradients have a direct relationship to molecular properties or are at least very useful in their determination, as the following examples show.

$\lambda = X_\mu$, a nuclear coordinate: The gradient $E_\lambda^{(1)}$ is then the (negative) force component acting on the nucleus. Knowledge of the gradient is very useful for structure relaxations to locate the minima of the potential energy hypersurface which define molecular isomers and conformers.

$\lambda = X_\nu, \mu = X_\kappa$: The second derivatives $E_{\lambda\kappa}^{(2)}$ completely specify the potential for the treatment of nuclear dynamics in the harmonic approximation, i.e. infrared and Raman spectra.

λ, μ = components of external electric or magnetic fields: $E_{\lambda\mu}^{(2)}$ is the polarizability or susceptibility tensor.

λ = component of the magnetic field, μ = component of the nuclear magnetic moment: $E_{\lambda\mu}^{(2)}$ gives the chemical shielding of NMR, and chemical shifts by comparison with a standard. We note in passing that the treatment of magnetic properties has caused many problems which are connected with achieving invariance with respect to the gauge of (magnetic) vector potentials [9].

The advantage of analytical gradient evaluations is again efficiency: the evaluation of the complete gradient with respect to all nuclear coordinates is faster than

the computation of the energy for SCF and DFT, and only about a factor 3 more expensive for MP2.

2.5 Electronic Excitations

The treatment of electronic excitation generally requires extended CI calculations which are not feasible for large molecules. If a computational procedure is envisaged for this purpose which is comparable in effort to SCF or DFT, one is led to consider Time-Dependent SCF and especially Time-Dependent DFT (TDDFT) [10]. Considering the molecule under the influence of an electric field with frequency ω, one computes $\alpha(\omega)$, the frequency dependent polarizability - technically a modification of the static polarizability computations mentioned above. Electronic excitations are then obtained as the poles of $\alpha(\omega)$, i.e. by putting $\alpha(\omega) = \infty$ in the corresponding equations. TDDFT appears to be more accurate than the SCF analogue [11] - usually called SCF-RPA (random phase approximation) - which in turn is closely related to a CI with the SCF reference and all single excitations (SCI). A final note: TDDFT can be expected to be of use (relative errors of a few tenths of an eV) only if excited states are sufficiently well described by single excitations - at least for the DFT functionals presently in use.

2.6 RI Methods (Resolution of the Identity)

Electronic structure calculations are essentially a struggle with the consequences of interelectronic interactions, i.e. the computation and processing of two-electron integrals $(\nu\mu|\kappa\lambda)$, Eq. (7), within the LCAO-MO approximation. In attempts to reduce the large number of two-electron integrals, one has tried to approximate products of basis functions, $f_\nu f_\mu$, by a set of atom-centered auxiliary (or fitting) basis functions g, ususally labelled by indices α or β:

$$\Delta_{\nu\mu} = f_\nu f_\mu - \sum_\alpha C_\alpha g_\alpha \approx 0 \ . \tag{18}$$

The late Jan Almlöf and coworkers have shown that the appropriate metric for (18) in the context of interelctronic interactions is given as [12]

$$||\Delta_{\nu\mu}||^2 = (\Delta_{\nu\mu}|\Delta_{\nu\mu}) = \int \Delta_{\nu\mu}(r_1) 1/r_{12} \Delta_{\nu\mu}(r_2) d\tau^6 = \min \ . \tag{19}$$

The condition (19) leads, after standard manipulations, to the following replacement

$$(\nu\mu|\kappa\lambda) \approx \sum_{\alpha\beta} (\nu\mu|\alpha)(\alpha|\beta)^{-1}(\beta|\kappa\lambda) \tag{20}$$

where $(x|y)$ is as in (7) or (19) and where $(\alpha|\beta)^{-1}$ denotes the inverse matrix. This approximation formally resembles the Resolution of the Identity in Hilbert space theory for non-orthogonal basis functions: hence the acronym RI.

The r.h.s. of (20) looks more complicated than the l.h.s., but using (20) may still be advantageous since it only involves two- and three-index quantities and no four-index quantities. The most pronounced gain in efficiency results if (20) is used for the approximate treatment of the Coulomb term J, eq. (12), giving the RI-J approximation

$$J \approx \sum_{\nu\mu} D_{\nu\mu}(\nu\mu|\alpha) \left[\sum_{\beta} (\alpha|\beta)^{-1} \left\{ \sum_{\kappa\lambda} (\beta|\kappa\lambda) D_{\kappa\lambda} \right\} \right] \tag{21}$$

This is employed profitably in DFT treatments where only J is present and E_{xc} is treated separately (Eq. (15)), which leads to the RI-DFT method discussed in [13]. No way has been found so far to exploit (20) in connection with exchange terms (13). On the other hand, quite pronounced gains in efficiency are achieved for MP2 calculations: the RI-MP2 approximation [14].

The RI approximation is of use only if auxiliary basis sets g_α are available for which the loss of accuracy incurred by (20) can be controlled. This is fortunately the case for the RI-DFT [13,15] and the RI-MP2 methods [16]: the errors introduced are without consequences, since they are much smaller than those that result anyway from typical basis sets. (For the experts: one achieves an accuracy of obout 50 $\mu H \approx 0.1$ kJ/mol per atom and the corresponding errors largely cancel for energy differences.)

2.7 Scaling Behavior

For treatments of large molecules it is essential to establish the so called "scaling behavior": the way in which computational effort increases with increasing molecular size. Theoreticians usually take the number of basis functions, N, as a measure of molecular size (the number of atoms would also do).

It is important to distinguish between *formal* and *asymptotic* scaling, as will be explained in this example. The total number of two-electron integrals $(\nu\mu|\kappa\lambda)$ clearly increases with N^4, the formal scaling. However in practice one can neglect sufficiently small integrals. Since the differential overlap $f_\nu f_\mu$ vanishes when the corresponding centers of basis functions are far apart, the number of $f_\nu f_\mu$ to be considered grows only in proportion to N, and the number of $(\nu\mu|\kappa\lambda)$ in proportion to N^2. This is the asymptotic scaling behavior for large molecules.

Analoguous considerations lead to the following results

Computational step	Scaling: formal → asymptotic
$(\nu\mu\|\kappa\lambda)$	$N^4 \rightarrow N^2$
RI-J (Eq. (21))	$N^3 \rightarrow N^2$
Quadrature	$N^3 \rightarrow N$
Linear algebra	$N^3 \rightarrow N^3$
MP2	$N^5 \rightarrow N^3$

Quadrature denotes here the numerical integration necessary for DFT to evaluate E_{xc} (which cannot be integrated analytically). Linear algebra includes the usual matrix operations: product, inversion, and diagonalization. Since the investigation of scaling behavior is a very active field of research [17,18,19,20] and since discussions are sometimes confusing, a few comments appear appropriate.

Quantum chemists have always tried to avoid unnecessary computations and thus achieve better scaling behavior. As an example we mention the timings for a series of Al clusters which include between 13 and 147 atoms, i.e. 200 to 3000 CGTO basis functions, for a gradient calculation within the RI-DFT method [13,21]. To save computer time O_h symmetry was used (in the comparison) although this is distorted by Jahn Teller effects in most cases. The total times never show the formal N^3 behavior. The CPU times increase like $N^{2.3}$ for the smaller cases and $N^{1.7}$ for the larger cases. Clusters of Al are densely packed systems and certainly cannot be considered as fortunate examples.

The scaling behavior is only one aspect of an algorithm. The exact Coulomb term, Eq. (7), and the RI-J approximation, Eq. (21), have the same asymptotic scaling - but the latter can be evaluated 10 to 100 times faster [13,15]. The N^3 scaling for linear algebra is not seen for these cases although matrix calculations are carried out. If computational effort is approximated as cN^x, the factor c can be as important or even more important as the exponent x over a wide range of N values.

Very impressive progress has been made in the development of 'linear scaling' methods [17,18,19,20] where one attempts to achieve $t_{CPU} \propto N$ asymptotically for large molecules. There are now algorithms available which scale better than N^2 (and often reach N) for all steps of energy or gradient calculations. An exception is exact exchange E_x, Eq.(13), for delocalized systems, which still appears to require N^2 effort [22]. Although it is not clear at present for which system size these methods offer an advantage as compared to the best procedures already available, they will play an important role in the future.

3 Computer Hardware: Another Zoo

3.1 PC's and Workstations

The computers that can be afforded by research groups, institutes, faculties, and actually most computation centers are based on microprocessors. These are truly impressive devices: with about 10 million transistors packed on 1 cm^2 they constitute almost complete computers (with CPU and memory, a primary cache with a few 100 kB) and deliver a performance of roughly 1 GIPS (10^9 instructions per second), dwarfing the best mainframes of three decades ago. The performance of microprocessors has been increased by a factor of two every 18 to 24 months over the last decade - and this trend will more or less continue over the next decade.

Microprocessors are only partly suited to scientific computing. Because of the considerable investment costs, microprocessor development has been driven by consumer electronics (games), PC's for homes and offices, graphics requirements and transaction machines in business. So far these computers could always also be used

Table 1. Timings of TURBOMOLE for representative molecules on a HP workstation (180 MHz, PA 8000); BF denotes the number of basis functions, MO the number of occupied MO's, G the molecular symmetry group, and N_{atom} the number of atoms.

Molecule / basis	G	Method	BF/MO	N_{atom}		
C_5H_5N / TZP	C_{2v}	SCF	150/21	11	energy	6.3 min
					gradient	1.4 min
$Ni(CO)_4$ / SVP	T_d	DFT	136/42	9	energy	1.7 min
					gradient	13 sec
$C_{19}H_{40}$ / SV	C_{2v}	MP2	251/77	59	energy +grad.	96 min
$(CoPH_3)_6$ As_{12}/ SVP	D_{3d}	RI-DFT	726/333	42	energy	33 min
					gradient	4.3 min
Fullerene C_{60} / 3-21G	I_h	DFT	540/180	60	energy	7.8 min
					gradient	58 sec
Acetyl Salecylic Acid / SV(P)	C_1	SCF	198/47	21	energy	25.0 min
					gradient	4.5 min
$Fe(C_5H_5)_2$ / SV	D_{5d}	MP2	131/48	21	energy	59 sec
/ SVP		SCF	214/48		energy	4.4 min
					gradient	39 sec
/ SVP		RI-DFT			energy	1.9 min
					gradient	21 sec
$Cu_{12}[P(C_2H_5)_3]_8S_6$/ SVP+ECP	C_{4h}	RI-DFT	1260/426	194	energy	210 min
					gradient	32.4 min
C_{70} / TZVP	D_{5h}	RI-MP2	1330/210	70	energy +grad.	49.3 h

for number crunching purposes in science and engineering.

The big success of decentralized computing – as opposed to using mainframes – came with UNIX workstations. These were open systems (hardware and software): all interfaces were standardized and their specifications published. One could combine parts from different manufacturers, opening the way to heavy competition and price reductions. PC's have recently become competitive with workstations in performance, even for typical number crunching applications. This has been greatly facilitated by the public domain system LINUX, a UNIX system for PC's and workstations. Windows and WindowsNT are so far hardly used for scientific computing. It is to be expected, however, that they will replace UNIX, first for the "low end" computers and later also for larger systems. This process is well under way and may proceed faster than expected.

A desktop system for scientific computing is typically equipped with 256 MB memory (at least 128 MB, up to 1 GB is usually possible) and disks with 4 GB or 9 GB capacity. Prices for these systems start below 10 000 DM. We have carried out computations with various small computers with the program system TURBOMOLE [23]. Some representative timings are collected in the Table 1 for a typical high end workstation. The same set of test cases (with very few exceptions since access was limited) has been run on other hardware which permits to compare their relative speed. A newer version is available via [23].

Relative Performance of some Workstations:
(larger numbers mean faster machines)

IBM RISC 3CT (67 MHz)	0.49
Pentium Pro (200 MHz)	0.52
IBM RISC SP2 node (120 MHz)	0.85
SGI (R 10 000, 190 MHz)	0.98
Pentium II (375 MHz)	0.96
DEC (personal workstation, 433 MHz)	0.96
HP PA8000 (180 MHz)	1.0
DEC (workstation, 600 MHz)	1.25

The reader should not forget that the above comparison is for TURBOMOLE, and here only on average with a standard deviation around 15%. Running other programs may lead to quite different relative efficiencies of the machines considered. For Pentium-based PC's we employed the "Portland Group" compiler, for all others those provided by the respective companies. The timings for the '375 MHz Pentium II' have been obtained with a 333 MHz processor driven at higher clock frequency.

3.2 Multiprocessor Machines

There is a clear trend towards machines with 2 to 8 CPUs in a single frame since this reduces costs for production and maintenance. Even larger machines contain 512 (or even more) processors and are designed for parallel processing of big problems, e.g. the "grand challenges". Parallel computers are at present the only way to reduce turn-around times for very demanding computations. However, scientists do not always get the hardware they would like. One has to work with the machines the engineers can construct or are told to construct by their companies: i.e. basically standard workstations with a fast connection network. Although these are very powerful and potentially useful tools, they are only reluctantly accepted since the burden of parallelizing codes to exploit this machinery lies entirely with the scientific programmer. It is also embarrassing that different computer architectures may require different parallelization strategies. In Quantum Chemistry the situation is further complicated since the methods and algorithms employed have not settled down and are still in a state of flux.

Despite all these problems a variety of codes is available in parallelized versions. In the next section it will be shown that impressive improvements in turn-around time have been achieved.

4 Calculating some Large Systems

4.1 Methods

We will try to give the reader a broad idea of applications carried out in Karlsruhe. This is appropriate for a feature article; a comprehensive survey of computational Quantum Chemistry would in any case be impossible in a few pages.

Let us first put the methods in order according to the effort typically required:

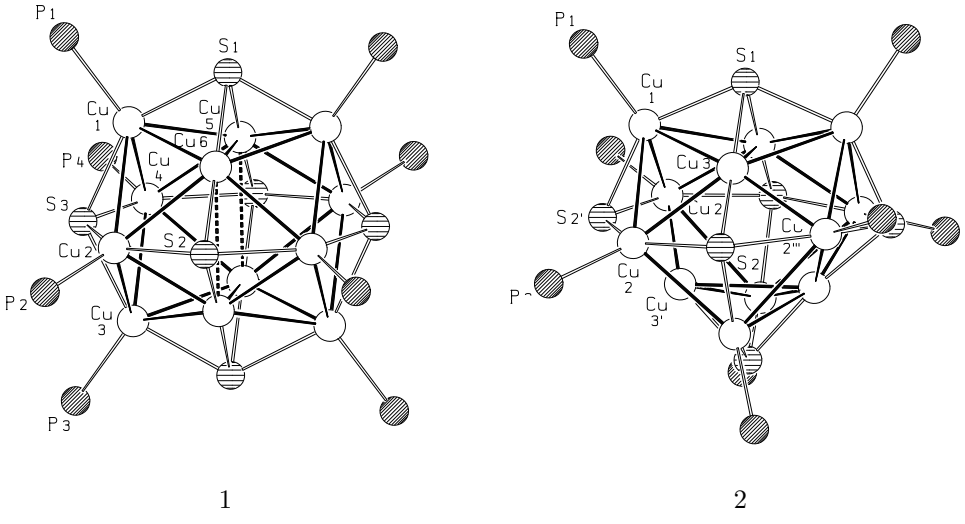
$$\text{Effort of MP2} > \text{RI-MP2} > \text{DFT}(J_{exact}) \geq \text{SCF} > \text{RI-DFT}.$$

This ordering applies to TURBOMOLE and most other programs where corresponding methods are implemented. DFT(J_{exact}) denotes usage of the exact Coulomb energy based on two-electron integrals, Eqs. (7), (8), and (12). Such calculations are more expensive than SCF since a quadrature is necessary in addition. RI-DFT is considerably more efficient than DFT(J_{exact}) or SCF – typically by a factor of 3 to 5 [13,15] – and is the method of choice for large systems. RI-MP2 is about 5 to 7 times faster than MP2 [14].

Molecular symmetry reduces computer times roughly according to the order of the molecular symmetry group, for TURBOMOLE at least. This makes it possible to calculate large molecules on small and inexpensive machines.

4.2 Ligand-stabilized Sulfur-bridged Copper Clusters [24]

Numerous sulfur or selenium bridged copper clusters have been synthesized and structurally characterized in the group of Dieter Fenske; accompanying theoretical treatments have been carried out especially to establish the energetics. S. Dehnen synthesized two structural isomers, type 1 and 2, Fig. 1, for $[Cu_{12}S_6(PR_3)_8]$. Whereas the type 1 structure is found for R=Et, and appears to be quite common, type 2 is known for R=^{n}Pr only. The calculations were started with the idea that a pronounced ligand effect would be responsible for this state of affairs: type 2 structures can better accomodate the bulkier ligands P^{n}Pr$_3$ (as compared to P Et$_3$). The following results were obtained.



1 2

Figure 1. Molecular structure types 1 and 2 for $[Cu_{12}S_6(PR_3)_8]$, the organic groups R attached to P are not shown.

(i) MP2 and DFT lead to virtually identical results for the model compound with R=H (larger R could not be treated by MP2). Type 1 is slightly more stable than type 2: by 2.4 kJ/mol (MP2) and 1.2 kJ/mol (DFT).

(ii) The type 1 and type 2 structure can easily accomodate either ligand, R=Et or R=^{n}Pr, Fig. 2. Type 1 is 22 kJ/mol (R=Et) and 24 kJ/mol (R=^{n}Pr) more stable than type 2.

Since the authors of the theoretical study see no compelling reasons to doubt the reliability of their findings, it was concluded that the structural types found in experiment are probably not determined by the energetics of isolated clusters alone and rather that kinetics plays the decisive role. The cluster with R=^{n}Pr precipitates already at -80°C and dissolves at higher temperature; for R=Et crystals form at -24°C. (The thermodynamically stable Cu_2S is obtained at room temperature in either case). To reconcile all aspects mentioned, it was proposed that structure 2, R=^{n}Pr, is kinetically stabilized at the low temperature where it exists.

This example involved very demanding calculations with structure determinations (in C_{4h} symmetry) for clusters with up to 266 atoms; timings are given in Table 1.

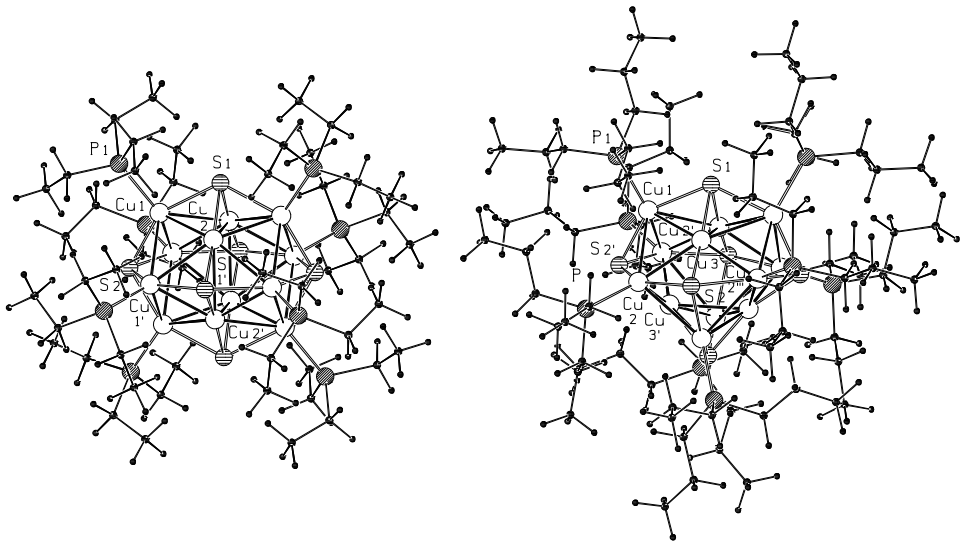
4.3 Cadmium Selenide Nanoparticles [25]

Clusters of semiconductor compounds such as CdSe often exhibit strongly size dependent electrical and optical properties. These materials could form the basis for new devices with considerable technological importance, e.g. light emitting diodes or electronic devices operating above GHz frequency. The behavior of the clusters is mainly governed by their electronic structure. Since the electrons are spatially confined to the cluster volume one expects and finds a pronounced "quantum size effect" which causes the size dependence of properties.

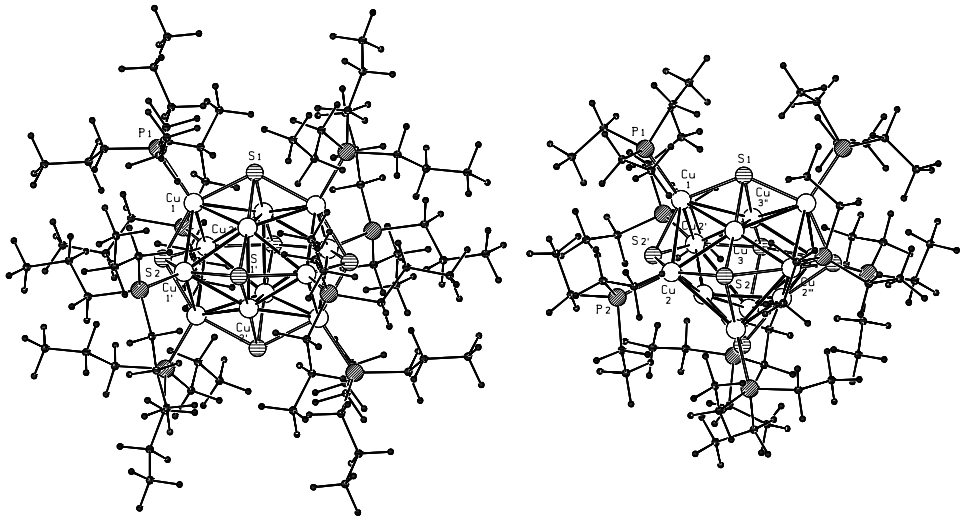
As a first step towards a detailed understanding of the quantum size effect the clusters shown in Fig. 3 have been investigated. The compounds have been mainly synthesized in the group of Fenske and are available as monodisperse materials in crystalline form (ionic clusters with the necessary counterions, of course). The stabilization of the clusters is achieved by protecting phenyl groups bonded to outer layer Se atoms.

Dipole allowed electronic excitation spectra are an important aspect of the electronic spectra. These have been computed within the TDDFT method employing the RI approximation [26]. The results are presented in Fig. 4. Since the two largest cluster could not be computed with the phenyl groups, these groups were replaced by H throughout for better comparison. Structure optimization - which show good agreement with experiment - has been carried out for the 294-atom cluster $[Cd_{10}Se_4(SePh)_{12}(PPh_3)_4]$; requiring 7 hours for an RI-DFT structure optimization cycle (energy + gradient) on a HP-PA 8000 (180 MHz).

The largest clusters treated have a diameter exceeding 1 nm: they are large enough to be "nanoclusters". However they are still too small to allow electronic excitations to be treated by band structure theory (with effective masses for holes and electrons). Quantum chemical calculations, although expensive, thus provide

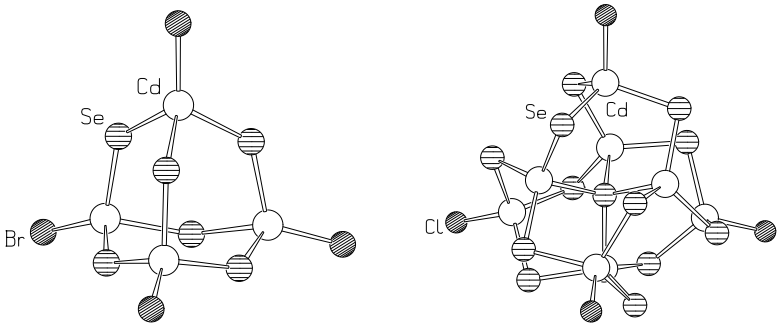


a) $[Cu_{12}S_6(PEt_3)_8]/C_{4h}$ $[Cu_{12}S_6(P^nPr_3)_8]/S_4$

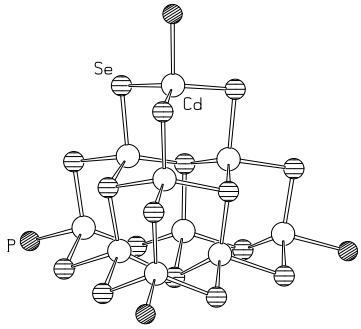


b) $[Cu_{12}S_6(P^nPr_3)_8]/C_{4h}$ $[Cu_{12}S_6(PEt_3)_8]/S_4$

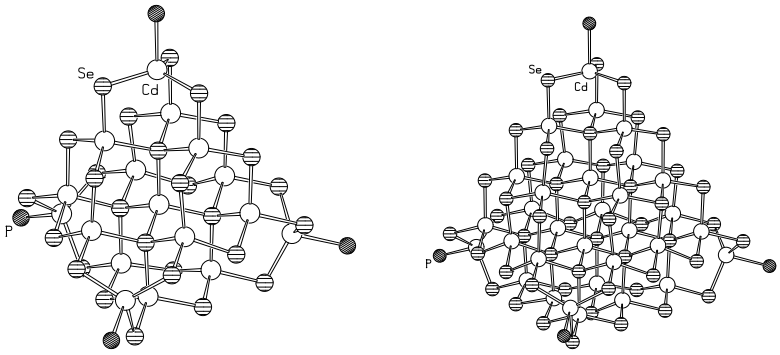
Figure 2. Computed RI-DFT structures of $[Cu_{12}S_6(PR_3)_8]$ for R=Et and ^{n}Pr. Type 1 clusters are on the left side (symmetry C_{4h}), type 2 on the right side (symmetry S_4); a) known compounds, b) 'hypothetical' clusters.



$[Cd_4(SePh)_6Br_4]^{2-}$ $[Cd_8Se(SePh)_{12}Cl_4]^{2-}$



$[Cd_{10}Se_4(SePh)_{12}(PPh_3)_4]$



$[Cd_{17}Se_4(SeH)_{24}(PH_3)_4]^{2+}$ $[Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4]$

Figure 3. RI-DFT cluster structures of $[Cd_4(SePh)_6Br_4]^{2-}$, $[Cd_8Se(SePh)_{12}Cl_4]^{2-}$, $[Cd_{10}Se_4(SePh)_{12}(PPh_3)_4]$, $[Cd_{17}Se_4(SeH)_{24}(PH_3)_4]^{2+}$, $[Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4]$; the ligands H and Ph attached to Se and P atoms are not shown.

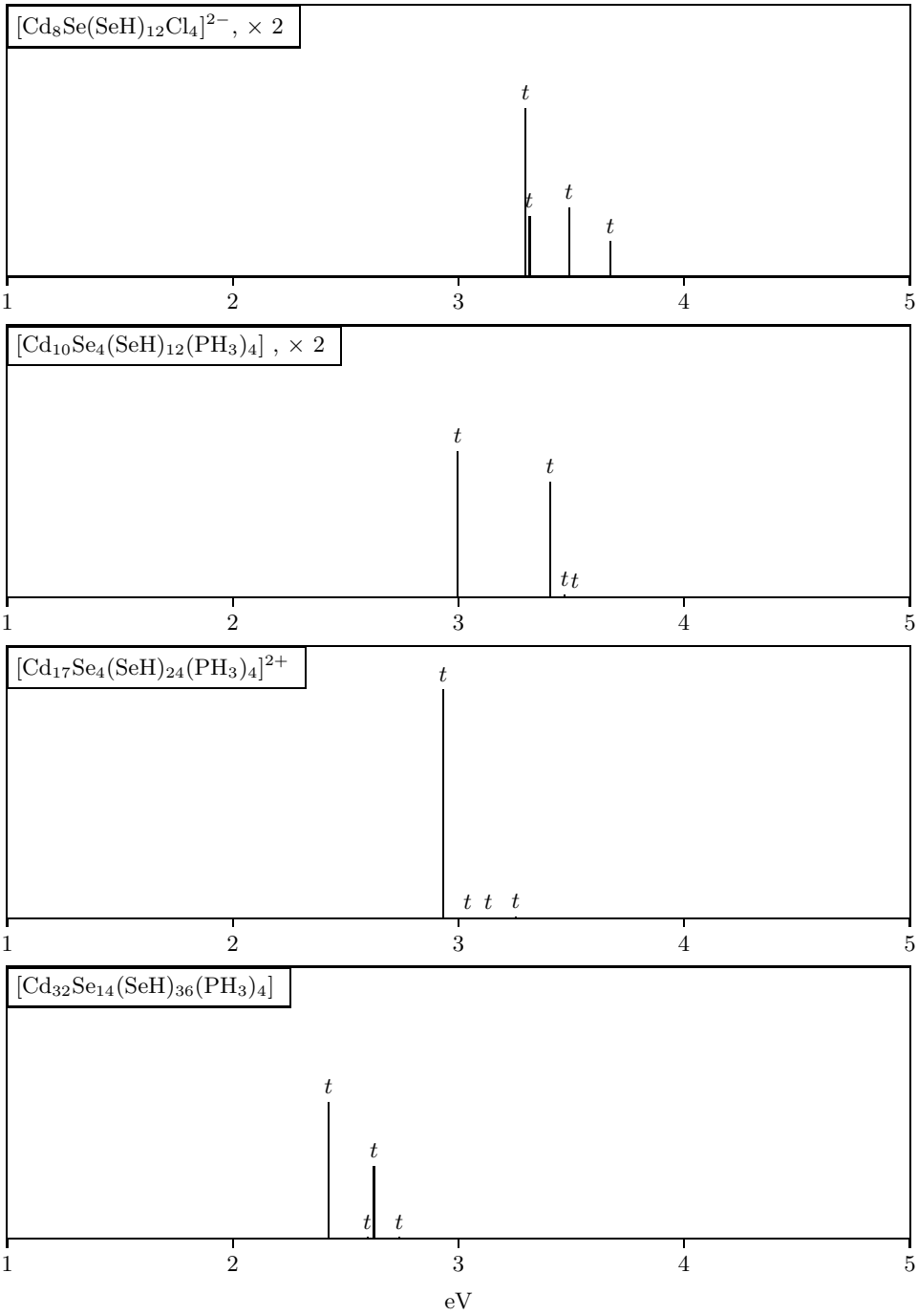


Figure 4. TDDFT electronic excitation spectra of $[Cd_8Se(SeH)_{12}Cl_4]^{2-}$, $[Cd_{10}Se_4(SeH)_{12}(PH_3)_4]$, $[Cd_{17}Se_4(SeH)_{24}(PH_3)_4]^{2+}$, $[Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4]$; the first dipole allowed transitions are shown.

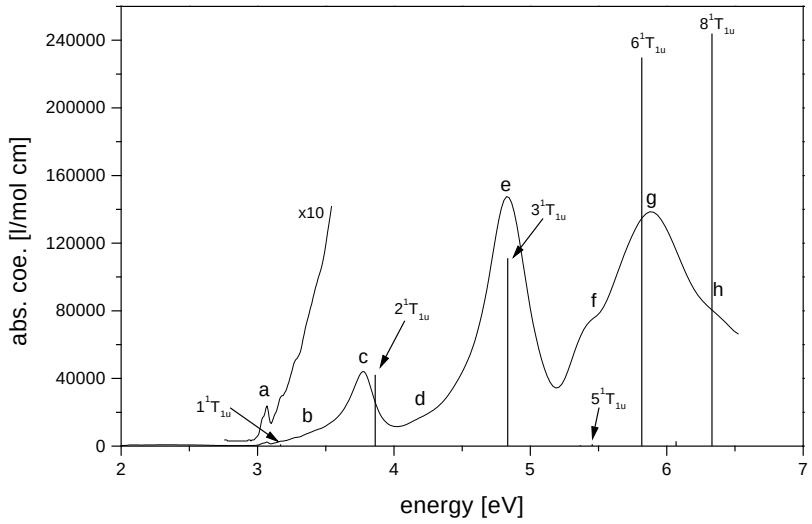


Figure 5. Absorption spectrum of C_{60} (I_h) in n-hexane at room temperature in comparison with the computed TDDFT excitation energies.

the only way so far to calculate such spectra for nanoclusters of this size; measurements could not be carried out so far. The calculated spectra are shown in Fig. 4. We observe that such large-scale calculations start to show convergence to the known bulk properties.

4.4 Fullerenes [27]

TDDFT [11,26] has been applied to compute electronic excitations of fullerenes C_{60} (I_h), C_{70} (D_{5h}), C_{76} (D_2), C_{78} (C_{2v}, D_3 and D_{3h}) and C_{80} (D_2). The fullerenes had been isolated and their spectra measured in solution (toluene, hexane). The calculations were carried out to assign the spectra as far as possible. Despite various uncertainties (solution versus gas phase, neglect of vibration), the level of agreement is good enough to allow assignment of the dominant spectral features. As a simple example we present a comparison of theory and experiment in Fig. 5. The computed excitation energies have all been increased by 0.35eV to compensate for the underestimation typical of TDDFT.

4.5 Parallelized Programs

It was only possible to calculate the large systems mentioned above on workstations and PC's by exploiting the molecular symmetry. Reducing the symmetry increases the computational demand; for example, in TURBOMOLE, going from D_{4h}, D_{4d}, T_d or O symmetry down to C_1 raises the time taken by a factor of 20. It is thus

impractical to compute systems of 300 atoms or so without symmetry on such workstations. Instead one needs parallel computers and parallel codes. The high symmetry cases treated on a single workstation could then be computed without symmetry restrictions but in comparable turn-around time with 8 to 32 parallel processors.

Parallel TURBOMOLE [28] achieves a very good speed-up in the dominant computational steps of SCF, DFT and RI-DFT calculations (energy and first order gradients). For the evaluation and processing of two-electron integrals as well as for the quadrature the speed-up is > 100 for 128 processors, ≈ 59 for 64 processors, and ≈ 30 for 32 processors. The RI-J algorithms even show a superlinear speed-up. The performance for a complete run is limited by linear algebra, however, which has not been efficiently parallelized.

Reliable estimates of the parallelization efficiency require a single processor run for comparison. The largest case for which this could be carried out was $[SiAl_{14}Cp^*_6]$, $Cp^* = (CH_3)_5$, with 165 atoms and 1365 CGTO basis functions. The following timings and speed-ups have been obtained in C_1 symmetry on an IBM SP2 (120 MHz) for a complete RI-DFT run.

Processors	Time/min	Speed-up
1	1131	1
8	135	9
16	71	16
32	43	26

At around 32 parallel processors one reaches the point of diminishing returns for the present program version. Even the large cases $[Cd_{10}Se_4(SePh)_{12}\ (PPh_3)_4]$ and $[Cd_{32}Se_{14}(SeH)_{36}\ (PH_3)_4]$ with up to 294 atoms and 2754 CGTO basis functions can be treated at the RI-DFT level in less than 4 hours on 32 processors.

5 Outlook

The ongoing dynamic development of methods and the continuing improvement of hardware have consequences which are easy to discern: Quantum Chemistry is rapidly becoming a standard tool of chemistry. In this respect it is following other techniques like NMR spectroscopy or X-ray scattering. There is an important difference which should be kept in mind. NMR and X-ray are the indispensable methods for qualitative and quantitative structure analysis. Quantum Chemitry has the capacity to be a universal tool to simulate all properties: spectra (ir, Raman, electronic, NMR), structures, energetics, intermolecular interactions, reactions, and so on.

Of course, this universal tool is still far off. Despite the progress theoreticians have made, the applicability of Quantum Chemistry is still restricted to specific cases. We just mention one problem: it would be highly desirable to develop efficient and reliable procedures to generate potential energy surfaces globally for larger molecules. This would allow the routine simulation of reactions and of the

temperature dependence of properties.

The progress in ab initio Quantum Chemistry also affects the computationally less demanding semi empirical and force field procedures. A better parametrization of these methods and an assessment of their accuracy becomes possible with the aid of detailed and reliable ab initio results often not available from experiment. One can further combine various methods in the treatment of a large molecule by means of embedding procedures [29], which may extend the applicability of ab initio methods to molecules in the range of 1000 to 10 000 atoms.

Solutions to many of the problems still limiting the applicability of present methods are in fact in reach or have been worked out in principle. With qualified manpower and sufficient support these will become routine in the near future.

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The work sketched in this article would not have been possible without the decisive contributions of the late Marco Häser. We remain greatly indebted to him. We also acknowledge the generous support of the University of Karlsruhe, the Fonds der Chemische Industrie and the DFG through SFB 195.

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